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THE EPA AIR MONITORING BANK PROPOSAL

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ABSTRACT

Specimen banking of air pollution samples has not been attempted because of the complexity of this type of environmental medium. Pollutants may exist in air as gases or particles or distributed in between these two states. Empirically, air pollutants may be categorized as volatiles, semivolatiles, or nonvolatiles based on vapor pressure. Since no single collection device exists for all three categories, very different monitoring technologies are required for each. The most promising approach for air specimen banking is to focus on the semivolatile fraction using a sampler that consists of a filter followed by a downstream sorbent material to collect gases. The combined solvent extract of both the filter and the sorbent can thereby be cryogenically preserved for retrospective analysis.

INTRODUCTION

Environmental specimen banking is becoming widely recognized as a complement to environmental monitoring.(1) By preserving environmental samples, future analysts will be able to characterize toxic pollutants that was not previously recognized as hazardous, or for which sufficiently accurate analytical methods were not available. The question has been asked, "Is this a new environmental pollutant or has it always been with us?(2) Specimen banking allows us to go back in time to do retrospective analyses to take advantage of newly emerging analytical methodologies that were not available at the time the specimens were initially collected and preserved.

Although there exist a number of environmental specimen banks in the United States, Germany, Canada, Sweden, and other countries for preserving samples of human tissue, biota, marine samples, food samples, and other specimen types, at the present time no adequate specimen bank exists for air samples. The reason for this is due to the complexity of airborne pollutants. Air pollutants may exist in association with particulate matter or as gases or something in between, i.e.; they may be gases absorbed on particles or in a gaseous state one time and a solid state another time.

So what type of sample or samples should we collect for preservation in an air specimen bank? The U. S. Environmental Protection Agency has been wrestling with this particular question and now plans to initiate a modest air specimen bank program in 1990. In this paper, I shall try to describe the rationale for the

EPA Air Specimen Bank Proposal and discuss the most promising means for collecting and preserving air samples available today.

CATEGORIZING AIR POLLUTANTS

Perhaps the best way to categorize air pollutants is by vapor pressure. Volatile compounds may be empirically defined as those having a vapor pressure $> 10^{-2}$ kPa, semivolatile compounds as those with a vapor pressure 10^{-2} to 10^{-8} kPa, and nonvolatile compounds as those with a vapor pressure of $< 10^{-8}$ kPa.(3) The use of vapor pressure as a method for categorizing air pollutants is sensible and is supported by our experience with monitoring of air pollutants. For example, volatile compounds are generally present in the atmosphere in the gaseous state only, semivolatile compounds may exist distributed between the gaseous and particle phases, while nonvolatile compounds are entirely associated with particulate matter. Some examples of common air pollutants for each type of category are shown in Tables 1-3.(4)

No single technique is available for sampling all three categories of pollutants at the same time; very different methods of sampling are required for each. A consideration of available sampling methodologies must be made to determine which are appropriate for specimen banking.

Nonvolatile Compounds

Nonvolatile compounds exist as airborne particulate matter and are collected by a filtration or impaction devices. Most commonly used is the high-volume air sampler in which particulate matter is

collected on glass or quartz-fiber filters.(5) The high-volume air sampler has been widely used throughout the United States and other countries for many years. It draws air at the rate of 1.1 to 1.7 m³/min through a 20 cm x 25 cm filter that is capable of removing nearly 100% of all particulate matter 0.3 μ m or greater in diameter. The filters are used for determining the concentration of total suspended particulate matter, trace metals and other elements, ionic species such as SO₄²⁻ and NO₃⁻, and polycyclic aromatic compounds containing five or more rings such as benzo-a-pyrene. EPA operates several hundred high-volume air samplers in its National Particulate Network and reports data on the following elements and compounds: Ba, Be, Cd, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn, As, Co, Cr, and benzo-a-pyrene.

As a general policy, the glass fiber filters collected in the National Particulate Network are preserved for 10 years in cardboard folders at room temperature. Although these preserved filters are occasionally useful for selective analysis such as determining the level of kepone resulting from unscrupulously manufacturing and disposal processes at a plant in Hopewell, Virginia(1) or for the reanalysis of some material as was recently done in our laboratory, it is doubtful that these filters would provide any additional meaningful information through a specimen banking program. Air pollutants with vapor pressures > 10⁻⁸ kPa are not sufficiently trapped on these filters and yet these are the compounds that would likely be of most interest to future environmentalists and analysts.

Volatile Air Pollutants

Up until several years ago, volatile air pollutants were largely trapped by sorbent materials such as Tenax-GC, a porous polymeric resin. These materials have generally suffered from a number of disadvantages including breakthrough of the more volatile compounds and artifact formation during thermal desorption for gas chromatography/mass spectrometry analysis. (4,6) More recently, the use of SUMMA-polished stainless steel canisters for collecting whole air samples has largely become the preferred method for collecting these types of compounds. (7) Canister sampling can be used for monitoring at remote sites through collection under vacuum, or sampling of a large air volume may be accomplished under pressure using electrically-powered pumps. Studies have shown that the interior surfaces of canisters passivated by the Moleetrics SUMMA® process allows storage of numerous compounds for periods of 30 days and longer without loss. (8) The use of canisters for collecting volatile compounds is especially attractive because of minimal artifact formation, no breakthrough loss, convenience of sampling at remote sites, easy cleanup procedures, and the possibility of multiple analyses of the collected air. However, it is unlikely that this type of methodology is suitable for specimen banking. It is difficult to conceive cryogenically storing six-liter canisters containing collected air for many decades. Consequently, the collection and preservation of whole air samples is not considered feasible for specimen banking purposes.

Semivolatile Air Pollutants

Semivolatile compounds represent the category of air pollutants that would be of greatest interest for specimen banking. As shown in Table 2, compounds in the vapor pressure range of 10^{-3} to 10^{-8} kPa include potentially toxic chemicals such as polycyclic aromatic compounds less than five rings; long-chain alkanes; and many oxygenated, chlorinated, and nitrogenous compounds. It is likely that many thousands of these compounds exist in ambient air, most of which have not been chemically identified.

The U. S. Environmental Protection Agency developed a high-volume sampler for efficiently collecting semivolatile compounds in the early 1980's.(9) It is commercially marketed as the PS-1 sampler by the General Metals Works, Village of Cleaves, Ohio. The PS-1 sampler consists of two sections, a filter for trapping nonvolatile compounds and a downstream sorbent bed using polyurethane foam or polymeric resins to trap pollutants that pass through or volatilize from the filter. The sampler operates at flow rates of up to 280 l/minute through both the filter and the sorbent bed with minimal pressure drop.

Solvent extraction of the combined filter and sorbent trap provides an excellent matrix for a variety of analytical techniques including gas chromatography/mass spectrometry, gas chromatography/matrix isolation infrared spectroscopy, and other modern techniques. It is likely that the solvent extracts can easily be cryogenically preserved in a specimen banking program.

THE AIR SPECIMEN BANK PROPOSAL

In 1990, EPA plans to implement a modest air specimen bank program using the PS-1 sampler. This program will operate in conjunction with the Toxic Air Monitoring System (TAMS) which is an experimental network for testing new air monitoring technologies operating in two U.S. cities, Houston, Texas and Boston, Massachusetts. In addition to the PS-1 sampler for collecting semivolatile compounds, other sampling methodologies are planned for the network in 1990 as shown in Table 4.

Solvent extracts of the PS-1 filter and sorbent (PUF or XAD) will be combined and sent to the cryogenic banking facilities at the National Institute of Standards and Technology located in Gaithersburg, Maryland. Initially, at least two 24-hour samples will be collected each quarter at each of the TAMS cities. In subsequent years, the network will be expanded to other urban locations and several background locations in the United States. Periodically, an aliquot from several selected samples will be analyzed by gas chromatography/mass spectrometry to determine whether any degradation has occurred for a number of target compounds. As we gain experience with the air banking program, we may modify the sample collection schedule and the quality assurance aspects as required.

TABLE 1. VAPOR PRESSURES OF SOME VOLATILE ORGANIC COMPOUNDS AT 25°C

Vapor Pressure kPa	Chemical Class		
	Chlorinated	Oxygenated or Nitrogenous	Normal Alkanes
100	Methyl Chloride Vinyl Chloride	Dimethylamine Phosgene Ethylene oxide	Butane
	Dichloromethane Chloroform Carbon Tetrachloride	Acrolein Acetone Acrylonitrile Methanol	Pentane Hexane
			Benzene
10	Tetrachloroethylene Chlorobenzene	1,4-Dioxane	Heptane Octane
1			Toluene Xylenes
10 ⁻¹	Monochlorotoluenes	Methylmethacrylate Benzaldehyde	Decane
			Styrene Mesitylenes
10 ⁻²	p-Dichlorobenzene Hexachlorobutadiene	Toluene-2,4-diisocynate Aniline Toxaphene Phenol	Dodecane

TABLE 2. VAPOR PRESSURES OF SOME SEMIVOLATILE ORGANIC COMPOUNDS AT 25°C

Vapor Pressure kPa	Chemical Class	Chlorinated	Oxygenated or Nitrogenous	Normal Alkanes	Aromatic
10 ⁻³		Tetrachlorobenzenes 2,4,5-Trichlorophenol Dichlorvos	Nicotine p-Chloroaniline p-cresol	Tetradecane	Naphthalene Biphenyl
10 ⁻⁴		Pentachlorobenzene	p-Nitroaniline	Hexadecane	Anthracene
10 ⁻⁵		Aroclor 1242 Pentachlorophenol Heptachlor	Diazinon Dibutylphthalate	Octadecane	Phenanthrene
10 ⁻⁶		Hexachlorobenzene Chlordane Aroclor 1260	Parathion Carbaryl Stearic Acid	Eicosane	
10 ⁻⁷		Dieldrin 2,3,7,8-Tetrachloro- dibenzo-p-dioxin	Anthraquinone	Hexacosane	Fluoranthene
10 ⁻⁸		DDT	Di(2-ethylhexyl)- phthalate		Bena(a)- anthracene

TABLE 3. VAPOR PRESSURES OF SOME NONVOLATILE ORGANIC COMPOUNDS AT 25°C

Vapor Pressure kPa	Chemical Class		
	Chlorinated	Oxygenated or Nitrogenous	Normal Alkanes
			Aromatic
10 ⁻⁹			Nonacosane
			Chrysene
10 ⁻¹⁰			Benzo(a)pyrene
10 ⁻¹¹			Benzo(ghi)perylene
10 ⁻¹²			
10 ⁻¹³			Coronene

TABLE 4. PROPOSED METHODOLOGIES

Compound Class	Proposed Sampling Protocol	Proposed Analysis Protocol	Estimated Deployment Date	Estimated Detection Limit
Volatiles Organics (Nonpolars)	SUMMA can	GC/MSD	10/89	0.10 ppb
Formaldehyde	2,4-DNPH	HPLC	10/89	0.10 ppb
Polar Organics	SUMMA can	GC/FID/MSD	1/90	0.50 ppb
Precursors	SUMMA can	GC/FID	10/89	0.50 ppb
Semivolatiles (Total)	Filter/XAD	GC/MS	1/90	0.1 ng/m ³
Semivolatiles (Particulates)	Denuder + Filter/XAD	GC/MS	1/90	0.1 ng/m ³
Biomonitoring	Filter/XAD	Bioassay	3/90	10 rev/m ³

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document.

Mention of trade names or commercial products does not constitute endorsement by the U. S. Environmental Protection Agency or recommendation for use.

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